

# PATENT SPECIFICATION

NO DRAWINGS

857,383



Date of Application and filing Complete Specification: Oct. 6, 1958.

No. 31877/58.

Application made in Germany on Oct. 26, 1957.

Complete Specification Published: Dec. 29, 1960.

**Index at acceptance:**—Classes 2(3), C2B20; 81(1), E1C(3A4:3B3:4A1:4B3:4B4:13); 95, A4(L: P); and 140, P3(B:F2:G4:G5).

**International Classification:**—A01n. C07d. C09d.

## COMPLETE SPECIFICATION

### New Dithia-Anthracene Derivatives and Fungicidal Compositions containing them

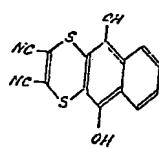
We, E. MERCK AKTIENGESELLSCHAFT, of Frankfurter Strasse 250, Darmstadt, Germany, a Germany Body Corporate, do hereby declare

the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to fungicidal agents.

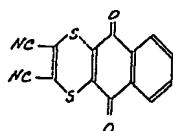
It has been found that 2,3-dicyano-1,4-dithia-anthrahydroquinone of the formula I

I



and the corresponding quinone of the formula II

II



have excellent fungicidal properties.

The new compounds have an essentially stronger fungicidal action than the best fungicides obtainable on the market at present.

The fungicidal action of the new compounds has been tested on a great variety of fungi, such as, for example, Rhizoctonia solani, Venturia inaequalis and Alternaria Spec. The average fungicidal action of the new compounds is nearly twice as strong as that of the best commercial products hitherto known such as TMTD (tetramethyl thiuram) disulphide, Captan (N-trichloromethyl-thio-tetrahydropthal

imide) and Ziram (N,N-dimethyl carbamic acid zinc salt).

The object of the invention is, therefore, to provide a fungicidal composition which contains in addition to a filler or carrier the 2,3-dicyano-1,4-dithia-anthrahydroquinone of the above shown formula I and/or the corresponding quinone of the above shown formula II.

An object of the invention is also the provision of the new compounds themselves.

The fungicides are well tolerated by plants. 2,3-dicyano-1,4-dithia-anthraquinone was worked up, for example, into a 80% spraying powder and used for spraying various vegetable wine and garden plants. None of the treated plants showed any phytotoxicity even when amounts of 1% had been used.

2,3-dicyano-1,4-dithia-anthraquinone can be prepared by reaction of the disodium salt of 1,2-dicyano-1,2-dimercapto ethene, with 2,3-dihalo-1,4-naphthaquinone. 2,3-dichloro-1,4-naphthaquinone is suitably used as the halogen compound. The reaction is expediently carried out in an inert solvent, such as, for example, methanol, ethanol, xylene or acetone. The reaction also proceeds by employing the reagents in suspension instead of solution. 2,3-dicyano-1,4-dithia-anthrahydroquinone can be prepared for example by catalytic hydrogenation of 2,3-dicyano-1,4-dithia-anthraquinone.

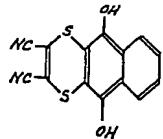
Compounds which have a certain similarity in their constitution with the new fungicides are described in U.S. Specification 2,547,723, British Specification 747,909 and German specification 876,018. Comparative tests have shown that these compounds have an essentially smaller fungicidal action than the fungicides according to the present invention.

The new compounds can be worked up in any form of application used for conventional pest control agents. According to known methods spraying liquors or dusting agents can be produced or the compounds can be added to paints or lacquers. In suitable sol-

BEST AVAILABLE COPY

- vents, the compounds according to the invention can also be used for the impregnation of textile fibres. It is also possible to work them up into solutions or emulsions used for spraying according to the aerosol process by applying the usual solvents known for this process. It goes without saying that mixtures of the new fungicides can be employed; the compounds according to the invention can also be used in admixture with other known pest control agents.
- In general the preparations contain not more than 95 percent by weight of active substance.
- EXAMPLES:**
15. 1. 3.7 g. of the disodium salt of 1,2-dimercapto-1,2-dicyan ethene and 4.6 g. of 2,3-dichloro-naphthoquinone are dissolved in alcohol. The reaction mixture reaches a temperature of about 40° C. by spontaneous heating.
20. The reaction is completed by subsequent boiling for half an hour. Cooling to about 10° C. and filtering with suction yield a NaCl-containing crude product. Purification is carried out by leaching with water and recrystallisation from ethylal or acetone. The 2,3-dicyano-1,4-dithia-anthraquinone thus produced crystallises as grey brown needles with a violet metallic lustre and melts at 220° C.
25. 2. 3 g. of 2,3-dicyano-1,4-dithia-anthraquinone are dissolved in 150 cc. of dioxan and hydrogenated with 2 g. of a platinum-carbon catalyst (10%). Thereupon, the catalyst is filtered off, the filtrate evaporated down, and the residue washed with petroleum ether. The undissolved portion is subsequently recrystallised from acetone. The 2,3-dicyano-1,4-dithia-anthrohydroquinone thus obtained melts upon rapid heating at 215° C.
- Yield 2.9 g.
30. 3. Spraying powder.  
80 parts of 2,3-dicyano-1,4-dithia-anthraquinone,  
10 parts of kaolin,  
10 parts of the sodium salt of the condensation product from oleic acid and methyl taurine commercial 32%, are ground to give the desired fineness. The powder thus produced can be sprayed or atomized in the form of dilute aqueous suspensions.
35. 4. Emulsion concentrate.  
40 parts of 2,3-dicyano-1,4-dithia-anthrohydroquinone,  
12 parts of polyoxy ethylene sorbitol ester of a mixture of fatty acids and resinic acids with a suitable sulphonate, such as commercial calcium dodecyl-benzene-sulphonate,
40. 3 parts of a sulphonated aliphatic polyester, and  
45. 45 parts of xylene are mixed together. The solution thus obtained is emulsified with water and can be sprayed or atomized.
50. 5. Liquid aerosol.
- 24 parts of 2,3-dicyano-1,4-dithia-anthraquinone or 2,3 - dicyano - 1,4 - dithia-anthrohydroquinone, 65  
76 parts of methylene chloride,  
50 parts of difluoro dichloromethane,  
25 parts of monofluoro trichloromethane and  
25 parts of commercial propane-butane 70 mixture are introduced into an aerosol pressure container for spraying.
6. Coating agent.  
15 parts of 2,3-dicyano-1,4-dithia-anthraquinone or 2,3-dicyano-1,4-dithia-anthrohydroquinone, 75  
10 parts of chalk,  
8 parts of zinc oxide,  
8 parts of iron oxide,  
5 parts of copper naphthenate,  
8 parts of linseed oil stand oil and  
16 parts of maleate resin are worked up with a total of 30 parts of a solvent to give a coating agent. It is expedient to mix first a small portion of the solvent (e.g. white spirit) with the mixture of ingredients and to add then the remaining portion of the solvent (white spirit with an addition of *n*-butanol, for example).
- WHAT WE CLAIM IS:—**
1. A fungicidal composition characterized by containing 2,3-dicyano-1,4-dithia-anthrohydroquinone of the formula I
- I
- 
- and/or the corresponding quinone of the 95 formula II
- II
- 
- and a filler or carrier.
2. 2,3-dicyano-1,4-dithia-anthraquinone of the formula
- 100
-

3. 2,3-dicyano-1,4-dithia-anthrahydroquinone  
of the formula



MEWBURN, ELLIS & CO.,  
70 & 72, Chancery Lane, London, W.C.2,  
Chartered Patent Agents.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1960.  
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which  
copies may be obtained.

BEST AVAILABLE COPY